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Full Length Article

Hydrophilic/hydrophobic surface modification impact on colloid lithography: Schottky-like defects, dislocation, and ideal distribution

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ABSTRACT

Nano-spheres lithography is actually considered as a powerful tool to manufacture various periodic structures with a wide potential in the field of nano- and micro-fabrication. However, during self-assembling of colloid microspheres, various defects and mismatches can appear. In this work the size and quality of single-domains of closed-packed polystyrene (PS), grown up on thin Au layers modified by hydrophilic or hydrophobic functional groups via diazonium chemistry was studied. The effects of the surface modification on the quality and single-domain size of polystyrene (PS) microspheres array were investigated and discussed. Modified surfaces were characterized using the AFM and wettability tests. PS colloidal suspension was deposited using the drop evaporation method. Resulted PS microspheres array was characterized using the SEM, AFM and confocal microscopy technique.

1. Introduction

Controllable creation of ordered surface pattern is now one of the most actual challenges in the various fields of advanced surface implementation [1–4]. Among the numerous techniques, which can be utilized for morphological or chemical surface pattering, the beam writing, soft or optical lithography, different kinds of thermodynamically induced instabilities can be mentioned [5–8]. However, the complexity of the preparation process combined with high initial equipment costs made these techniques unfavourable in many cases. An alternative approach consists in the application of nano or microspheres self-assembling processes, which can naturally occur and lead to the formation of ordered 2D or 3D structures [9–11]. In particular, microspheres lithography, also known as the colloid or natural lithography, attracts great attention due to its "low" cost, the simplicity of the process and good controllability [12,13]. Created by colloid lithography 2D ordered arrangements present a high potential for applications in different fields such as surface enhanced phenomena [14,15], biomolecules separation [16] or creation of quantum dots or rods [17,18].

Colloid lithography can produce an ordered pattern on large area in several minutes, but this technique has two significant drawbacks -(i) restricted palette of available surface geometries and (ii) predisposition to defect formation limiting perfect periodicity down to micrometer-sized areas [19]. Thus possible use of this technique for the fabrication of defect-free structures on large domains represents a challenge [20]. Typical techniques of spheres deposition include the drop-deposition or spin-coating techniques. Many works were devoted to the optimization of deposition conditions by concentration variation, substrate tilting, solvents variation, addition of surfactant or modification of spheres surface [21–26]. Alternative deposition methods, such as electrophoretic Langmuir–Blodgett and floating self-assembly Langmuir–Blodgett coatings were also proposed with the aim to increase single domain size and pattern quality [27–34].

In the case of drop-deposition, detailed studies on formation of closed packed microspheres array indicate that attractive capillary forces and convective transport of the nanospheres are the main factors affecting the self-assembly process, while the orderliness and quality of the obtained arrays are considerably influenced by the rate of solvent evaporation [35–37]. On the other hand, it is well known that the drop evaporation dynamic depends on surface wettability [38,39] and roughness [40,41] too. In this work, the impact of preliminary surface modification on the size and quality of closed-packed polystyrene (PS) single-domain was studied. The surfaces of thin Au layers were modified by arenediazonium tosy-

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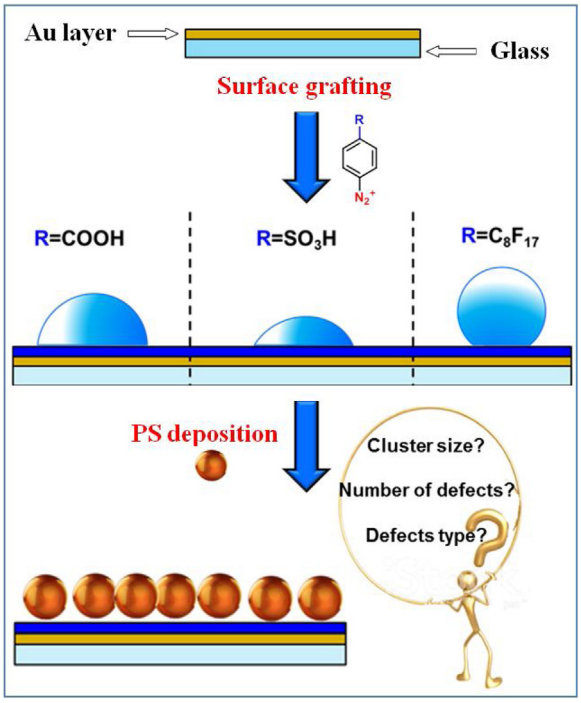

Fig. 1. Schematic representation of Au surface grafting and their properties tuning with the aim to investigate further deposited PS array quality.

lates ADTs, containing the hydrophilic or hydrophobic substituents and the impact of surface wettability (contact angle) changes on the size of "single-domain" area as well as on the appearance of defects in the PSs packing was investigated.

2. Experimental

2.1. Materials

Gold thin layers with the thickness ca 20 nm were deposited onto glass surface (Thermo Scientific), covered by adhesive titanium layer (thickness ca 10 nm), using thermal evaporation method. Targets for metals deposition (purity of metals 4 N) were purchased from Safina. 4-carboxybenzenediazonium tosylate, 4-sulfobenzenediazonium salt and 4-(heptadecafluorooctyl)benzenediazonium tosylates were prepared according to published procedure [42]. PS suspension (spheres diameter 500 nm) was purchased from Alfa Aesar.

2.2. Samples preparation

The 4-carboxyphenyl, 4-sulfophenyl, and 4-(heptadecafluorooctyl)phenyl organic functional groups (OFGs) were grafted spontaneously by soaking of the freshly obtained Au layers in 2 mM freshly prepared solutions of corresponding arenediazonium tosylates (ADTs) in deionized water for 10 min (for 4-(heptadecafluorooctyl)benzenediazonium tosylate mixture of water/ethanol (3/1) was used) [43]. After modification the metal substrates were sequentially rinsed under sonication with deionized water, ethanol, and acetone for 10 min and dried in desiccator for 3 h. PS suspension was drop deposited and slowly evaporated on modified Au surface, under the careful control of temperature (40 °C) at air.

2.3. Measuring techniques

For characterization of the sample surface and nanomechanical mapping before and after the surface modification, the peak force AFM technique was used. Surface mapping was performed with Icon (Bruker) set-up. Confocal microscopy images were taken using the Olympus Lex laser microscope. Contact angles were measured by goniometer Surface Energy Evaluation System (Masaryk University, Czech Republic) with distilled water (drop volume – 2 μL). The scanning electron microscopy (SEM) was used for the study of morphology of PS microspheres array on pristine and modified Au layers. SEM images were taken using LYRA3 GMU, Tescan, CR set-up with 10 kV accelerating voltages and previous samples coating by 10 nm thick Pt layer.

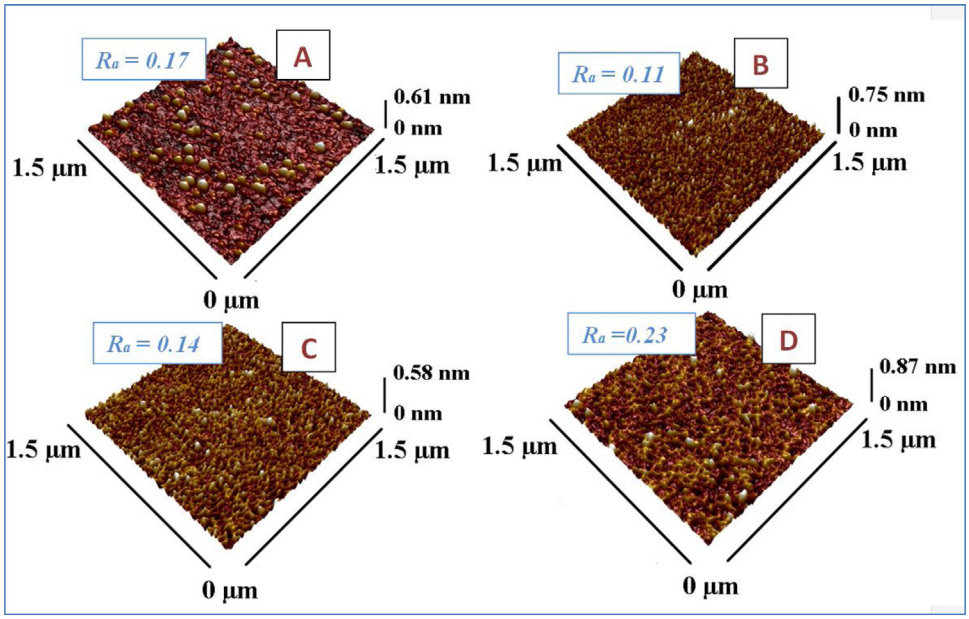

Fig. 2. Surface morphology of pristine (A) and grafted with organic compounds (B: $-SO_3H$; C: –COOH; D: $-C_8F_{17}$) Au layers.